

## PROBLEM-SOLVING TACTICS

### Calculation of Degree of Ionization, pH of Weak Acid/Base and Equilibrium Concentrations of All Species

Knowing the ionization constant of the weak acid/base and its initial concentration, the degree of ionization and equilibrium concentrations are calculated as follows:

**Step 1.** Write the balanced equation for dissociation in the solution.

**Step 2.** Assume  $\alpha$  as the degree of dissociation (or  $x$  as the amount dissociated) and calculate the equilibrium concentrations.

**Step 3.** Substitute the equilibrium concentrations in the expression for  $K_a$  or  $K_b$ , and calculate  $\alpha$  (or calculate the amount dissociated  $x$  and then  $\alpha = x/c$  where  $c$  is the initial concentration).

As already discussed in Art. 7. 18, if  $\alpha$  is very small, we can calculate  $\alpha$  directly using the expression  $\alpha = \sqrt{k_a / c}$

**Step 4.** Knowing  $[H^+]$ , calculate pH or knowing  $[OH^-]$ , calculate pOH. Then  $pH = 14 - pOH$ .

#### (a) Criteria for Precipitation

**Case I:** When  $K_{ip} < K_{sp}$ , then solution is unsaturated in which more solute can be dissolved.

**Case II:** When  $K_{ip} = K_{sp}$ , then solution is saturated in which no more solute can be dissolved.

**Case III:** When  $K_{ip} > K_{sp}$ , then solution is supersaturated and precipitation takes place. When the ionic product exceeds the solubility product, the equilibrium shifts towards left hand side, i. e., increasing the concentration of undissociated molecules of the electrolyte. As the solvent can hold a fixed amount of electrolyte at a definite temperature, the excess of the electrolyte is thrown out from the solution as precipitate.

Thus, for the precipitation of an electrolyte, it is necessary that the ionic product must exceed its solubility product.

**(b)** Calculation of the remaining concentration after precipitation: Sometimes, an ion remains after precipitation, if it is in excess. Remaining concentration can be determined, e.g. .

$$(i) [A^+]_{left} = \frac{K_{sp}[AB]}{[B^-]}$$

$$(ii) [Ca^{2+}]_{left} = \frac{K_{sp}[Ca(OH)_2]}{[OH^-]^2}$$

$$(iii) [A^{n+}]_{left}^m = \frac{K_{sp}[A_m B_n]}{[B^{m-}]^n}$$

$$\text{Percentage precipitation of an ion} = \left[ \frac{\text{Initial conc.} - \text{Left conc.}}{\text{Initial conc.}} \right] \times 100$$

## POINTS TO REMEMBER

Ostwalds dilution law for weak electrolyte	$K_a = \left( \frac{\alpha^2}{1-\alpha} \right) \left( \frac{1}{V} \right)$
Acid & Bases : Arrhenius theory	(i) An Arrhenius acid is a substance which furnishes the hydrogen ion (H <sup>+</sup> ions) in an aqueous solution (ii) An Arrhenius base is a substance which furnishes the hydroxyl (OH <sup>-</sup> ) ions in an aqueous solution
Bronsted Lowry theory	(i) A Bronsted acid is proton donor (ii) Bronsted base is proton acceptor.
Lewis concept	(i) A Lewis acid is an electron pair acceptor (ii) A Lewis base is an electron pair donor.
Some basic concept	pH scale: $\text{pH} = -\log [\text{H}^+]$ Autoionization of water: $K_w = [\text{H}^+][\text{OH}^-]$ . $K_a[\text{H}_2\text{O}] = K_w/[\text{H}_2\text{O}]$
Homogenous Ionic equilibria Acid base equilibrium	(a) Strong acid/base $[\text{H}^+] = \frac{c}{2} + \sqrt{\frac{c^2}{4} + K_w}$ ; $c = \text{conc. of (acid)}$ (b) pH due to polyprotic weak acids (c) Weak monobasic acid/base $[\text{H}^+] = \sqrt{K_a \cdot c}$ (if $\alpha < 0.1$ ) (d) Mixture of S. A. /W. A. (e) Mixture of W. A. /W. A. $\text{H}^+ = \sqrt{K_1 c_1 + K_2 c_2}$ (f) Buffer solutions: $\text{pH} = \text{p}K_a + \log \left( \frac{\text{salt}}{\text{acid}} \right)$ $\text{pOH} = \text{p}K_b + \log \left( \frac{\text{salt}}{\text{base}} \right)$ (g) Salt hydrolysis – (W. A. /S. B. ) $\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a + \log c)$ (W. B. /S. A. ) $\text{pH} = \frac{1}{2}(\text{p}K_w - \text{p}K_b - \log c)$ (W. A. /W. B. ) $\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a - \text{p}K_b)$ (h) pH due to hydrolysis of polyprotic acid. Complexation equilibrium $\{\text{M}^{n+} + m\text{Lig} \rightleftharpoons [\text{M}(\text{Lig})_m]^{n+}\}$ $\left\{ K_{sb} = \frac{[\text{M}(\text{Lig})_m]^{n+}}{[\text{M}^{n+}][\text{Lig}]^m} \right\}$
Heterogeneous equilibrium	Solubility of sparingly soluble salt' $(\text{AB}, \text{AB}_2, \text{A}_x\text{B}_y) K_{sp} = (\text{S}^{x+y})\text{X}^x\text{Y}^y$

Solubility Product	$K_{sp} = [xS]^x [yS]^y = x^x \cdot y^y (S)^{x+y}$ <p><b>Special Cases:</b></p> <p>(i) 1: 1 type salts: Examples: AgCl, AgI, BaSO<sub>4</sub>, PbSO<sub>4</sub>, etc. <math>S = \sqrt{K_{sp}}</math></p> <p>(ii) 1: 2 or 2: 1 type salts: Examples: Ag<sub>2</sub>CO<sub>3</sub>, Ag<sub>2</sub>CrO<sub>4</sub>, PbCl<sub>2</sub>, CaF<sub>2</sub>, etc.  <math>S = \sqrt[3]{K_{sp} / 4}</math></p> <p>(iii) 1: 3 type salts: Examples: Al<sub>3</sub>, Fe(OH)<sub>3</sub>, Cr(OH)<sub>3</sub>, Al(OH)<sub>3</sub>, etc.  <math>S = \sqrt[4]{K_{sp} / 27}</math></p> <p>In presence of common ion effect –</p> $K_{sp} = S'(S' + c)$ <p>(i) <math>[A^+]_{\text{left}} = \frac{K_{sp} [AB]}{[B^-]}</math></p> <p>(ii) <math>[Ca^{2+}]_{\text{left}} = \frac{K_{sp} [Ca(OH)_2]}{[OH^-]^2}</math></p> <p>(iii) <math>[A^{n+}]_{\text{left}}^m = \frac{K_{sp} [A_m B_n]}{[B^{m-}]^n}</math></p> <p>Percentage precipitation of an ion = <math>\left[ \frac{\text{Initial conc.} - \text{Left conc.}}{\text{Initial conc.}} \right] \times 100</math></p>
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